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Phthalocyanine Dyes and Pigments

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In 1927, de Diesbach and von der Weid (*1*) obtained a new insoluble blue compound by reacting o-dibromobenzene, cuprous cyanide, and pyridine at 200°C., in a sealed tube. The product they obtained was thought to be $[C_6H_4(CN)_2 + C_5H_5N]_2Cu$. However, because of an error in determining the nature of the product and analytical difficulties characteristic of compounds of this series, erroneous conclusions were drawn as to its identity. In all probability, the chemical was copper phthalocyanine.

In 1928, at the Grangemouth works of Messrs. Scottish Dyes, Ltd., in the manufacture of phthalimide by passing ammonia into molten phthalic anhydride in an iron vessel, it was observed that the molten imide contained traces of a dark-blue substance. After a preliminary examination of the compound, the problem of determining its structure was referred to Linstead. The work of Linstead and his students (*2*) resulted in a complete picture of the structure of this important new class of color compounds; their findings have since been confirmed by an x-ray investigation that was made by Robertson (*3*).

Although the phthalocyanines are closely related structurally to chlorophyll and hemin, there is no evidence that they occur in nature. The fundamental nucleus of the natural coloring matters of the chlorophyll and hemin series is porphine, represented by the structural formula at the left in Figure 1. The degree of resonance in the porphine derivatives is undoubtedly very high; therefore, the distribution of the conjugated

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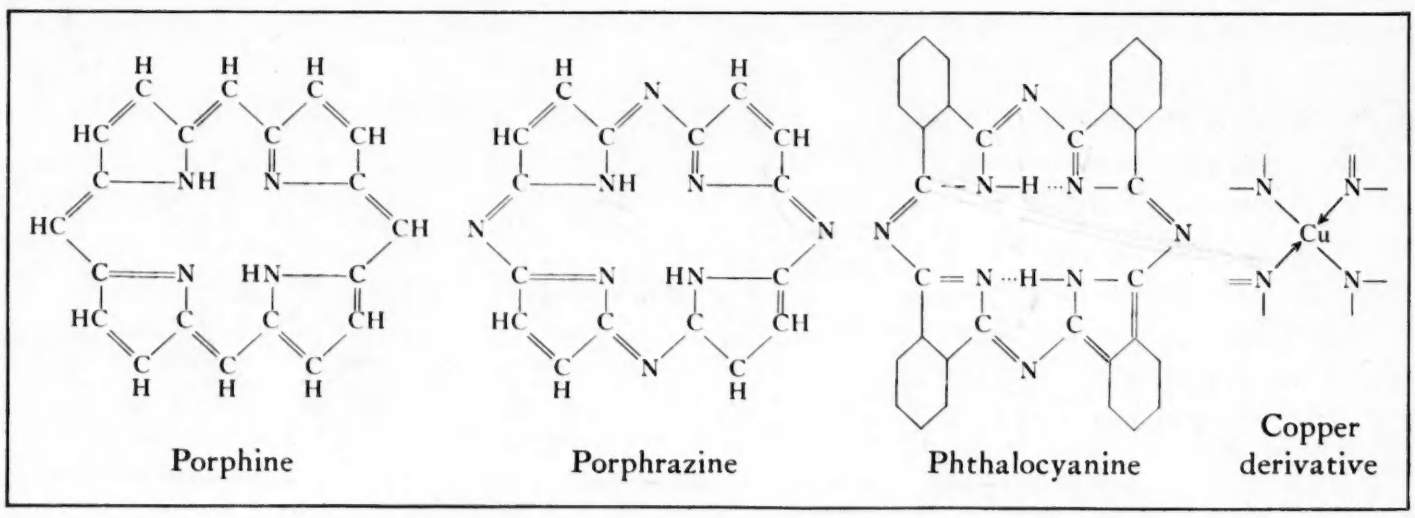

FIGURE 1—*Structure of porphine and some of its derivatives.*

double-bond system shown in the formulas, Figure 1, is entirely arbitrary.

If the four methine groups that join the four pyrrole nuclei in the alpha positions were replaced by nitrogen atoms, tetrazaporphine (otherwise known as porphrazine) would be obtained. However, this compound is known only in the form of its derivatives, as, for example, tetrabenzoporphrazine, which was called "phthalocyanine" by Linstead. Many metal derivatives of phthalocyanine have been synthesized; with copper as the example, the central part of the molecule is represented at the right in Figure 1. Robertson has proved that the phthalocyanine molecule is planar.

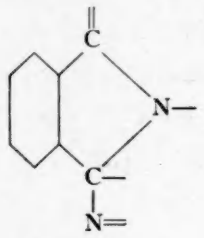

FIGURE 2

Compounds that are capable of producing an isoindole ring containing an "extracyclic" nitrogen atom, Figure 2, will, in general, form phthalocyanines when reacted with metals or metal derivatives; the reaction may occur under a wide variety of attendant conditions.

Each step in the series of reactions shown in Figure 3 is well known, and each compound represented will react with various metals and metal derivatives to produce metal phthalocyanines. The first two (phthalic anhydride and phthalimide) require ammonia, urea, or a similar compound, as a reactant in order to produce the isoindole ring that contains the extracyclic nitrogen. It will be noted that o-cyanobenzamide, when heated above its melting point (172°C.), produces the compound, iminophthalimidine, which is actually a derivative of isoindole.

Phthalocyanine can easily be made on a laboratory scale by reacting phthalonitrile with sodium amylate to form disodium phthalocyanine (phthalocyanine with the two central hydrogen atoms replaced with two sodium atoms); treatment of this compound with hot water will yield the metal-free phthalocyanine. Phthalonitrile, when produced according to the scheme in Figure 3, is rather difficult to obtain in the pure state. It is, therefore, convenient in laboratory preparation to react o-cyanobenzamide with magnesium in naphthalene at 245°C., and to treat the product with acid to obtain metal-free phthalocyanine. However, o-cyanobenzamide is too easily hydrolyzed in sodium amylate to produce phthalocyanines by this method. Phthalocyanine may also be prepared by reacting molten phthalonitrile with hydrogen sulfide at 170-180°C. (*4*).

Phthalonitrile, when reacted with cuprous chloride at 170°C., will form copper phthalocyanine and cupric chloride. If the reaction is conducted at about 210°C., copper monochlorophthalocyanine is obtained. Metal derivatives of phthalocyanine have been prepared by the reaction of metal-free phthalocyanine with a metal such as magnesium, or a metal derivative such as cupric chloride, in boiling quinoline.

Diphenylmaleinitrile, when heated at 275°C., in the presence of etched magne-

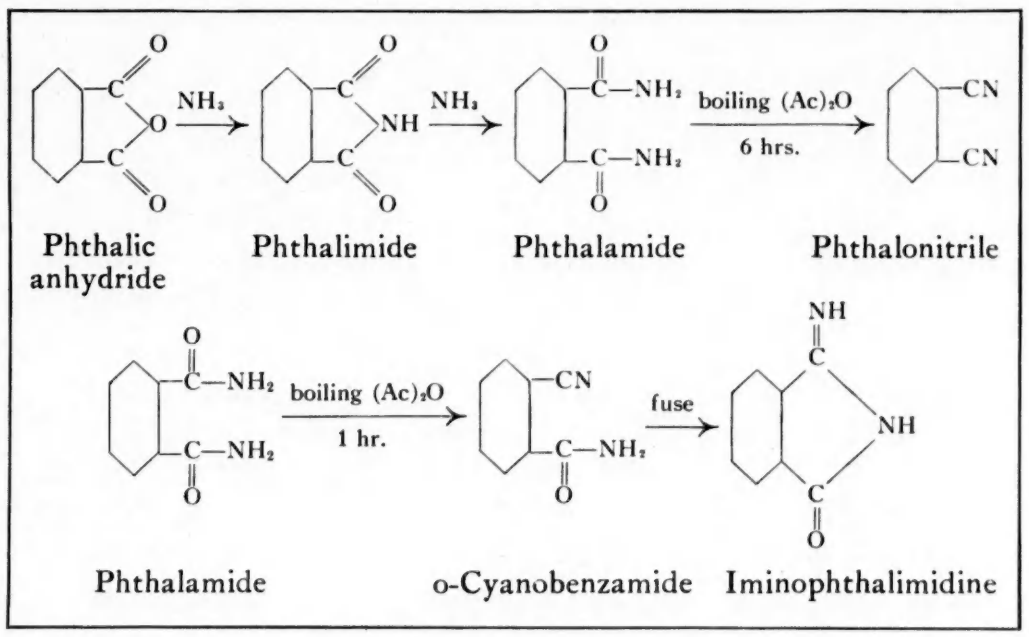

FIGURE 3—*Reactions involved in the preparation of phthalonitrile and iminophthalimidine from phthalic anhydride.*

REACTIVITY OF METALS AND METAL DERIVATIVES WITH PHTHALONITRILE

REACT READILY	REACT LESS READILY	DO NOT REACT
Sodium	Sodamide	Sodium Hydroxide
Sodium Amylate	Sodium Methylate	Sodium Phenylate
Magnesium	Sodium Ethylate	Sodium Chloride
Copper	Potassium Amylate	Potassium Hydroxide
Cuprous Chloride	Calcium Amylate	Magnesium Chloride
Cupric Chloride	Magnesium Oxide	Antimony Chloride
Ferric Chloride	Antimony (catalytic action)	Phosphorus Chlorides
Nickel	Cuprous Oxide	Iodine
Nickel Chloride	Cupric Oxide	
	Cupric Acetate	

sium turnings, will form magnesium octaphenylporphrazine. When 1,2- or 2,3-naphthalonitrile and powdered zinc are heated to 310°C., the metal naphthalocyanine is obtained. Methyl lithium will react with phthalonitrile in cyclohexanol, at 200°C., to give tetrabenzotriazaporphine. Methylmagnesium iodide will react with phthalonitrile in alcohol, to give magnesium tetrabenzotriazaporphine.

The reactions mentioned are only a few of the many variations that are known. Most of these are very exothermic and the use of solvents, such as pyridine, quinoline, chloro- and bromo-naphthalenes, is helpful in controlling and facilitating the reactions. The o-halogenobenzonitriles, o-sulfobenzonitriles, and o-dihalogenobenzenes have also been used in this type of reaction, but it is necessary with these compounds to include a cyanide, such as cuprous cyanide, to supply the necessary CN radical for the formation of the isoindole ring that contains the extracyclic nitrogen; this, in turn, yields the phthalocyanine.

Nuclear substitution products of almost any variety of the compounds already mentioned may be used provided they are compatible with the method of synthesis chosen. It is necessary that the nitrile groups be attached to adjacent carbon atoms. Terephthalonitrile, homophthalonitrile, o-xylylenedicyanide, o-cyanocinnamonitrile, and 2,2′-dicyanodiphenyl will not react to give porphrazine derivatives. In the heterocyclic class, porphrazine derivatives have been produced from the ortho dinitriles of thiophene, thionaphthene, pyridine, and pyrazine. Negative results were obtained in the pyrrole, isooxazole, and isotriazole series. A practical guide as to whether the dinitriles will yield porphrazine derivatives is the capacity of the corresponding o-dicarboxylic acids and their diamides to form anhydrides and imides.

The table, "Reactivity of Metals and Metal Derivatives with Phthalonitrile," lists, according to their reactivity with phthalonitrile, some of the metals and metal derivatives that have been tested in the preparation of phthalocyanines.

The manner in which a metal is held to the phthalocyanine molecule is by no means an arbitrary matter. This question has been decided by applying the tests of volatility, and solubility in organic media (*5*). Sodium, potassium, calcium, barium, and cadmium phthalocyanines differ from the other metal phthalocyanines in that they are very insoluble and are incapable of sublimation. On treatment with acids, and, in some cases, with hot water, these compounds also readily liberate metallic ions and form metal-free phthalocyanine. It is, therefore, concluded that the metal-nitrogen linkages in these five compounds are electrovalent.

The other metal phthalocyanines are covalent in combination with co-ordinate

valencies (see copper derivative, Figure 1). One of the reasons for this conclusion is the fact that copper phthalocyanine is stable in the vapor phase at 580°C., which eliminates the possibility of the metal being held only by co-ordinate bonds. The fact that the zinc compound is covalent and the cadmium compound is electrovalent is in keeping with Fajan's principle, which states that in the same periodic group of metals the tendency to form covalent compounds decreases with the increase in atomic number.

The phthalocyanines can be quantitatively oxidized to phthalimide and ammonia by the use of ceric sulfate in an acid solution. They are very resistant to alkali, and are soluble to some extent in boiling quinoline, pyridine, and chloro- and bromonaphthalenes. Phthalocyanine has been halogenated and sulfonated quite successfully. The Friedel-Crafts reaction to introduce alkyl groups has been unsuccessful. In general, the reactivity of the fused benzene rings is of a fairly low order, but their extreme insolubility presents the most serious problem.

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